JOURNAL OF CATALYSIS 36, 238–239 (1975)

Conformational Studies of Chemisorbed Hydrocarbon on Zeolite Catalyst

Simple alkene radical cations have been observed by electron spin resonance spectroscopy in both liquid flow systems (*1*) and in solid zeolitic matrix (*2*). Similar hyperfine splitting constants were obtained for both preparative techniques. However, very little experimental information is available for the nonplanarity of the open-chain alkene cation radicals and its internal rotation barrier about the central three-electron $\mathrm{C}\dot{-}\mathrm{C}$ bond. We have, therefore, studied the ESR spectra of various alkene cation radicals utilizing synthetic H-Mordenite zeolite as matrix and using its intrinsic Lewis acid sites presumably as oxidative agent (*3*).

Prior to the present investigation, only the radical cations of highly methyl-substituted ethylenes have been observed. No simple open-chain alkene cation radicals with α-hydrogen have been reported. We now wish to report the results of our studies on butene-2 molecules chemisorbed on the H-Mordenite zeolitic surface.

Synthetic H-Mordenite is first calcinated with oxygen for 1 hr at 500°C to remove impurities, then activated under vacuum for 2 hr at the same temperature. After cooling to room temperature, the zeolite catalyst was transferred to standard EPR 3 mm sample tubes. 2-Butene vapor was chemisorbed on H-Mordenite catalyst at 77 K. EPR measurements were carried out on a Varian X-band 4502 spectrometer with temperature control accessories.

The ESR spectrum of *cis*-butene-2 at −30°C chemisorbed on H-Mordenite matrix is shown in Fig. 1. It consists of a septet separated by 16.3 G. This large hyperfine splitting, which was assigned to the two identical methyl groups, is comparable to the 17.5 G methyl splittings in the 2,3-dimethylbutene cation radicals (*3*), but is much smaller than the predicted value (22 G) based on the $Q^{\mathrm{H}}_{\mathrm{CH_3}}$ for the planar durene cation (*4*) ($Q^{\mathrm{H}}_{\mathrm{CH_3}} = 44$ G). A triplet with spacing 8.2 G was assigned to the α-hydrogens. A similar spectrum was obtained for *trans*-butene-2 chemisorbed on the H-mordenite surface with identical hyperfine splittings and the results are listed in Table 1.

The observation of a small splitting at the α-position in both *cis*- and *trans*-butene-2 cation radicals ($a_\alpha^{\mathrm{H}} = 8.2$ G), in comparison with the closed-ring cyclopentene cation radical case ($a_\alpha^{\mathrm{H}} = 14.5$ G), suggests that open-chain alkene cation radicals have a nonplanar conformation (*5*). An INDO calculation (*6*), based on the reported structure of *cis*-butene-2 as determined by microwave spectroscopy (*7*) has been carried out. The observed hydrogen hyperfine splittings are in good agreement with conformation with an out-of-plane

TABLE 1

Observed Proton Hyperfine Splittings of Simple Alkene Cation Radicals on Zeolite

Alkene	$\lvert a_\beta^{\mathrm{H}}\rvert$ (G)[a]	$\lvert a_\alpha^{\mathrm{H}}\rvert$ (G)[a]	Temp (°C)
cis-Butene-2	16.2	8.2	−30
trans-Butene-2	16.2	8.2	−50
Cyclopentene[b]	37.0	14.5	−125
2,3-Dimethylbutene[b]	17.5	–	25

[a] Estimated error is 0.4 G.

[b] Ref. (*2*).

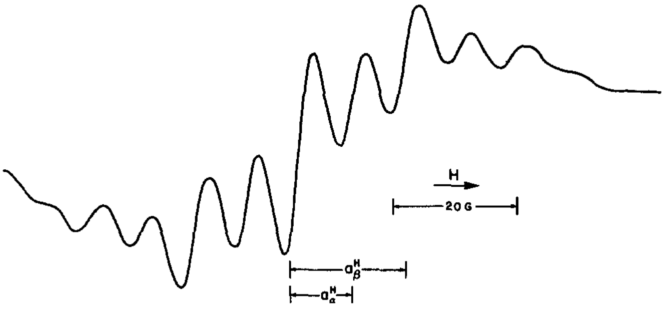

FIG. 1. The ESR spectrum of chemisorbed *cis*-butene-2 on H-zeolon molecular sieve at −30°C.

torsional angle of 30° at equilibrium. The potential curve is quite close to Merer and Mulliken's calculation (*8*) with an internal rotation barrier of 1 kcal/mole. Such a small potential barrier implies that the possibility of isomerization may involve cation radicals as intermediates in parallel with the usual protonic carbonium ion mechanism.

ACKNOWLEDGMENTS

Helpful discussion with former Mobil colleagues Drs. P. L. Corio and D. H. Olson as well as the skillful technical assistance of Mr. O. M. Epifanio are gratefully appreciated. Thanks are also due to the Quantum Chemistry Program Exchange, Indiana University, for making the INDO program available. The author expresses his gratitude to the Mobil Research and Development Corporation for permission to publish this paper.

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Received July 24, 1974